The Astrophysical Journal, 679:1670–1679, 2008 June 1

CALCULATIONS ON THE FORMATION RATES AND MECHANISMS FOR C_nH ANIONS IN INTERSTELLAR AND CIRCUMSTELLAR MEDIA

Eric Herbst
Departments of Physics, Astronomy, and Chemistry, The Ohio State University, Columbus, OH 43210; herbst@mps.ohio-state.edu

and

Yoshihiro Osamura
Kanagawa Institute of Technology, Atsugi 243-0292, Japan
Received 2008 January 2; accepted 2008 February 23

ABSTRACT

The rate coefficients for the radiative attachment reactions between the radicals C_nH ($n = 2$–8) and electrons have been calculated with the aid of quantum chemistry using a phase-space theory in which strong coupling exists among the ground and any excited anion electronic states with the same spin. The results confirm that the process increases in efficiency with the size of the radical. For $n \geq 6$, the rate coefficients lie at the collisional limit, in agreement with earlier estimates. For $n = 4,5$, the new results are larger than the old estimates. The calculated rate coefficient for $C_4H + e^-$ is now much too large to explain the current observed abundance ratio of C_4H^-/C_4H in IRC +10216 and L1527 and its upper limit in TMC-1. It is quite possible that electronic coupling is weak, and that so-called "dipole-bound" and other states must act as doorways to radiative attachment. We have also calculated potential surfaces for dissociative attachment starting with the "carbenes" H_2C_{2m} ($m = 2$–4) and leading to the syntheses of the anions $C_{2m}H^-$.

Subject headings: astrochemistry — ISM: abundances — ISM: molecules

1. INTRODUCTION

Based on laboratory spectroscopic work (McCarthy et al. 2006; Gupta et al. 2007; Thaddeus et al. 2008), four negatively charged molecular ions, known as anions, have been recently detected in the interstellar and circumstellar media. The anion C_4H^- has been observed in the envelope of the carbon-rich star IRC +10216 (Cernicharo et al. 2007) and in the protostar L1527 (Sakai et al. 2008; Agúndez et al. 2008), the anion C_8H^- in IRC +10216 and the cold interstellar core TMC-1 (Remijan et al. 2007; Brünken et al. 2007; Kawaguchi et al. 2007), the anion C_6H^- in all three of these sources (McCarthy et al. 2006; Kasai et al. 2007; Sakai et al. 2007), and most recently, the anion C_3N^- in IRC +10216 (Thaddeus et al. 2008). The detections of anions have emphasized the need for a better understanding of the chemistry of negative molecular ions.

Anions can be produced via a variety of mechanisms. In laboratory discharges, dissociative attachment is a well-known process in which an electron reacts with a neutral species AB to produce a negative ion plus a neutral species; e.g.,

$$e^- + \mathrm{AB} \longrightarrow \mathrm{A}^- + \mathrm{B}. \quad (1)$$

Since the binding energy of an electron to a neutral species, known as the electron affinity, is typically smaller in energy than a chemical bond ($\geq$4 eV), dissociative attachment is normally endothermic, as in

$$e^- + \mathrm{HCCCN} \longrightarrow \mathrm{CCCN}^- + \mathrm{H}, \quad (2)$$

which is endothermic by 1.3 eV (Graupner et al. 2006). In order for dissociative attachment to be exothermic and so occur at low temperatures, there must exist weak chemical bonds in the precursor neutral. Several such processes have been discussed in the astrophysical literature. Petrie (1996) realized that the formation of CN^- could occur via the exothermic reaction

$$e^- + \mathrm{MgNC} \longrightarrow \mathrm{CN}^- + \mathrm{Mg} \quad (3)$$

from the precursor neutral MgNC, which has been detected in IRC +10216. Shortly thereafter, Petrie & Herbst (1997) showed that the anion C_3N^- could be produced exothermically from the unusual isomer HNCCC:

$$e^- + \mathrm{HNCCC} \longrightarrow \mathrm{CCCN}^- + \mathrm{H}, \quad (4)$$

if not from normal cyanoacetylene (HCCCN). Recently, Sakai et al. (2007) calculated that the anion C_6H^- can be formed from the "carbene" H_2C_6:

$$e^- + \mathrm{H_2C_6} \longrightarrow \mathrm{C_6H}^- + \mathrm{H}, \quad (5)$$

a reaction that is exothermic by a small amount (16 kJ mol^{-1}; 1 kJ mol^{-1} = 120.3 K). We have calculated by methods discussed below that the corresponding reaction to form the anion C_8H^-,

$$e^- + \mathrm{H_2C_8} \longrightarrow \mathrm{C_8H}^- + \mathrm{H}, \quad (6)$$

is exothermic by 47 kJ mol^{-1}. Note, however, that the similar reaction to form the anion C_4H^- is endothermic by 26 kJ mol^{-1}, so that this anion cannot be produced from the carbene H_2C_4 at low temperatures (Sakai et al. 2007).

Many years before dissociative attachment was considered for astronomical sources, Herbst (1981) had suggested that radiative attachment of electrons to neutral species could occur efficiently in the cold interstellar medium for polyatomic neutrals containing more than $\approx$3–4 atoms and large electron affinities (>2–3 eV). At the time, some experimental work on radiative attachment had

been previously reported, although for fluorine-containing molecules of little interstellar interest (Woodin et al. 1980). In this process, an electron simply attaches to a neutral species A by capture:

$$e^- + \mathrm{A} \longrightarrow \mathrm{A}^- + h\nu, \quad (7)$$

with the excess energy emitted as radiation. Herbst (1981) focused on neutral radicals such as C_4H, C_3N, and larger analogs known to have large electron affinities, and estimated that if electrons could stick to neutrals with near 100% efficiency, they could reach an abundance of 1% of the neutral precursors. The argument was based on a simple statistical theory known as phase-space theory, in which angular momentum is rigorously conserved. In the phase-space theory, the rate of attachment depends strongly on the density of vibrational states of the anion at a vibrational energy equal to the electron affinity of the neutral, and this density of states depends in turn on the size of the anion and the electron affinity of the neutral. The theory was discussed in more detail in subsequent papers (Herbst 1985; Petrie & Herbst 1997) and used to calculate rate coefficients for the radiative attachment of electrons to bare carbon clusters when it was thought that negative molecular ions of the type C_n^- might be present in diffuse interstellar clouds (Terzieva & Herbst 2000). In addition, a calculation of the rate coefficient for the radiative attachment to form the anion C_3N^- was undertaken by Petrie & Herbst (1997), and simple estimates were made for the formation of negative ions of the class C_nH^- with $n \geq 7$ in a model of the chemistry of IRC +10216 (Millar et al. 2000).

Following the interstellar detection of the first molecular anion, C_6H^-, Herbst estimated radiative attachment rate coefficients for a variety of smaller ions ($n = 2$–6) in the C_nH^- family (Millar et al. 2007). The results showed that the rate coefficient depends strongly on the value of n; for $n = 2$ it is negligibly slow, while for $n = 6$, the process occurs at its collisional limit. The very low rate coefficient for the formation of C_2H^- is in agreement with current negative efforts to detect it (Agúndez et al. 2008). Calculated attachment rate coefficients, along with estimated rate coefficients for the destruction processes of negative ions, were put into chemical models of a variety of sources by Millar et al. (2007) and subsequently for IRC +10216 only by Remijan et al. (2007). From these results, it would appear that although the radiative attachment rate coefficient for $C_4H + e^-$ estimated via the phase-space theory is significantly below the collisional limit, it is still too large to explain the observations assuming that the destructive processes are handled correctly in the chemical models. A model performed by Cernicharo et al. (2007) for IRC +10217 showed that the C_4H^- abundance is best fit with a radiative attachment rate coefficient 1–2 orders of magnitude below the phase-space estimate (see also Agúndez et al. 2008). A similar conclusion can be drawn from the new results for this anion in L1527 (Sakai et al. 2008; Agúndez et al. 2008). For the larger anions C_6H^- and C_8H^-, the model of Millar et al. (2007) predicts the anion-to-neutral abundance ratios quantitatively in TMC-1 and IRC +10216, although the absolute column densities in the latter source are less well explained. The later model of IRC +10216 by Remijan et al. (2007) improved the column densities of these anions and neutrals at the expense of their abundance ratios. In a paper on the detection of C_6H^- in the protostellar source L1527, Sakai et al. (2007) were the first to include the formation of this anion by dissociative attachment of the carbene H_2C_6 as well as by radiative attachment. They estimated that the mechanisms could be comparable in efficiency for L1527. No detailed model of this source including negative ions has yet been reported, although we have just finished one (Harada & Herbst 2008).

The rate coefficients for formation of the C_nH^- anions by radiative attachment used in the recent models are highly uncertain because the needed detailed information concerning vibrational density of states and radiative emission rates was not available. In this paper, we report more detailed phase-space calculations of radiative attachment rate coefficients for $n = 2$–8 with vibrational frequencies and radiative intensities supplied by quantum chemical methods. There are several reasons to pursue these calculations. First, it is important to see if the poor agreement with the C_4H^- abundance can be improved and the good agreement for C_6H^- and C_8H^- maintained by employing a more detailed calculation. Second, if agreement is worsened, then a more complex approach to radiative attachment might need to be undertaken, possibly involving "doorway" states (Güthe et al. 2001).

Phase-space theory assumes that once an unstable negative ion, known as a "complex" or "temporary negative ion," is formed, all vibrational states in all accessible electronic states can be formed rapidly with restrictions only on electron spin. The process has been termed "fast internal conversion" (Güthe et al. 2001). The net result is typically that the ground electronic state dominates, because it has the highest density of vibrational states at the initial energy of the complex. Once the internal conversion has occurred, the complex can be stabilized by emission of a photon. If internal conversion is slow, however, the complex likely loses the electron before undergoing internal conversion, unless there are resonances.

Studies of the electronic spectroscopy of negative molecular ions reveal, in agreement with theory, that weakly bound excited and diffuse states of anions known as "dipole-bound" states, in which the electron is loosely bound to the neutral, exist if its dipole exceeds 2.0–2.5 Debye (Güthe et al. 2001). These states can lie slightly below the energy of the neutral species; with rotational and vibrational energy, there then exist Feshbach resonance states in the continuum of the anion. Figure 4 in Güthe et al. (2001) shows such a situation for the anion of linear C_3H_2. Feshbach resonances have also been studied in scattering experiments between electrons and polar neutrals (Christophorou 1983). The resonances can provide the "doorways" for radiative attachment if they are sufficiently long-lived and lie only slightly above the neutral species in energy. On formation, they can then mediate the relaxation to lower valence states of the anion. Once the anion lies in the valence system, it is possible that internal conversion to the ground electronic state can occur rapidly. If radiative attachment occurs solely by the resonance mechanism followed by rapid conversion, the phase-space result for the rate of radiative attachment must be reduced by the fraction of thermal energy space occupied by Feshbach resonances, as depicted in Figure 182 of Herzberg (1966). Of course, reality can be even more complex.

Whatever the merit of the Feshbach mechanism for thermal attachment, it must be remembered that dipole-bound states exist only if the neutrals have sufficiently high dipole moments. The fact that the radical C_4H has a small dipole moment of 0.9 Debye in its ground state whereas the C_6H and C_8H radicals have dipole moments exceeding 5 Debye (Brünken et al. 2007) means that dipole-bound states based on the ground-state configuration cannot aid in the radiative attachment of C_4H, unlike the case of the larger species. As discussed later in the paper, however, there is a low-lying excited electronic state of the C_4H radical that does possess a large dipole moment, and this state can mix with the ground state (Woon 1995; Hoshina et al. 1998).

In the following section, we briefly discuss the quantum chemical methods used in the calculations. We then review the salient

aspects of the phase-space theory of radiative attachment and report some calculations on dissociative attachment. The final section contains our results for radiative attachment and a discussion of their astronomical importance.

2. QUANTUM CHEMICAL METHODS

We have calculated the molecular structures and vibrational frequencies of the neutral C_nH species and their anions C_nH^- ($n = 2$–8) in both the ground electronic state and in the lowest excited state, the energies of which have also been determined. In addition, we have calculated the radiative intensities for the anionic normal modes. Finally, we have calculated the potential energy surfaces for dissociative attachment reactions involving the carbenes H_2C_n ($n = 4, 6, 8$) and leading to the C_nH anions in order to look at these reactions in more detail. In the quantum chemical calculations, we have used the hybrid density functional B3LYP method (Becke 1993; Lee et al. 1988) with the aug-cc-pVTZ basis functions (Dunning 1989) so that we can describe the anionic states with high accuracy. The relative energies were corrected by zero-point vibrational energies without scaling. All calculations were carried out with the GAUSSIAN 98 program package (Frisch et al. 2001).

3. THEORY OF RADIATIVE ATTACHMENT

In statistical theories of chemical reactions without barriers, the system passes through a complex (†), often located at a potential minimum, in which all details of the reactants are erased except for the total energy of the system and, in phase-space theories, its angular momentum. Here the complex is the temporary negative ion formed with an energy slightly above that needed for detachment (the electron affinity). Radiative attachment can be depicted in a phase-space viewpoint by the following series of processes:

$$\mathrm{A}(j) + e^- \longrightarrow (\mathrm{A}^- \dagger)(j), \quad \text{complex formation } (k_1) \tag{8}$$

$$(\mathrm{A}^- \dagger)(j) \longrightarrow \mathrm{A}(j) + e^-, \quad \text{complex auto-detachment } (k_{-1}) \tag{9}$$

$$(\mathrm{A}^- \dagger)(j) \longrightarrow \mathrm{A}^-(j') + h\nu, \quad \text{radiative stabilization } (k_r), \tag{10}$$

where j and j' represent states of rotational angular momentum. Here it is assumed that the electronic angular momentum does not couple with j and that only s-wave scattering occurs. The rate coefficients for the three processes are labeled k_1 ($\mathrm{cm^3\ s^{-1}}$) for formation of the complex, k_{-1} ($\mathrm{s^{-1}}$) for auto-detachment of the electron, and k_r ($\mathrm{s^{-1}}$) for radiative emission of a photon to stabilize the complex. If one makes the steady-state assumption for the concentration of the complex, then the overall rate coefficient for radiative attachment $k_{\mathrm{ratt}}(j)$ is given by the simple expression

$$k_{\mathrm{ratt}}(j) = \frac{k_1(j)k_r(j)}{k_{-1}(j) + k_r(j)}. \tag{11}$$

Since none of the three rate coefficients depends strongly on j (Herbst 1985), this index can be dropped.

The cross section σ for formation of the complex formed from reactant A in any state j and s-wave electrons is given by the expression

$$\sigma = \frac{\pi\hbar^2}{2\mu E}, \tag{12}$$

where μ, the reduced mass, is essentially the electronic mass, and E is the collisional energy (Herbst 1985). The rate coefficient for this process, k_1, is then given by the translational thermal averaging of the cross section multiplied by the collisional speed. Substituting for the assorted constants yields (Petrie & Herbst 1997)

$$k_1 = 4.982 \times 10^{-7}[T(\mathrm{K})/300]^{-0.5}. \tag{13}$$

Since the only temperature dependence in the expression for the radiative attachment rate coefficient stems from k_1, $k_{\mathrm{ratt}} \propto T^{-1/2}$.

To form the complex with the electronic symmetry of the ground state, we must include a factor G, which is the ratio of the electronic degeneracy of the ground state of the anion to the overall degeneracy of the reactants. For example, if an electron (^2S) collides with the radical C_4H ($^2\Sigma$), the electronic states of the linear anion that can be produced have symmetry $^3\Sigma$ and $^1\Sigma$. Since we then assume that all states of the same symmetry can interact with one another, and that the ground state is favored in the $^1\Sigma$ manifold of states, if other such states exist, because of its high density of vibrational states, then the probability for the complex to be formed in the $^1\Sigma$ ground state is 1/4. If we wish to consider formation into the system of excited triplet states, then we can do so; here $G = 3/4$ and, once again, because of its high density of vibrational states, this factor essentially refers to the lowest triplet state. The total radiative attachment rate coefficient would then be the sum of singlet and triplet contributions.

For the cases of C_5H and C_6H, the ground state of the linear radical has $^2\Pi$ symmetry, and reaction with an s-wave electron leads to anion states in linear geometry of $^3\Pi$ and $^1\Pi$. If the anion has a nonlinear geometry, the Π states correlate with sets of A' and A'' states in planar (C_s) symmetry. For C_6H^-, neither of the two states correlating with reactants has the symmetry of the linear $^1\Sigma$ ground state of the anion, and we assume that this state is formed by rapid vibronic coupling with the $^1\Pi$ state such that it occurs statistically, with a value G of 1/8. The first excited state of C_6H^- is calculated to have $^3A''$ symmetry, and the structure of the anion in this state is nonlinear. Here $G = 3/8$. For C_5H, the anion is nonlinear in both the ground triplet and excited singlet states. If the triplet state can be accessed from reactants, $G = 3/8$. The lowest excited singlet state lies very close to the ground state; if we consider this state as well, it will have $G = 1/8$.

The formula for k_{-1} is based on microscopic reversibility; its derivation is given in the Appendix of Herbst (1985; see their eq. [A8]) in a discussion of radiative association, which involves a more complex set of angular momenta. Reducing the formula there to remove orbital angular momentum, since the scattering is s-wave, and to remove the angular momentum of one of the two reacting partners, we get the simple expression that

$$k_{-1} = c/\rho, \tag{14}$$

TABLE 1
ELECTRON AFFINITIES UTILIZED

Radical	Electron Affinity (eV)	Source
C_2H	2.956	Experiment (T98)
C_3H	1.93	Theory (this work)
C_4H	3.558	Experiment (T98)
C_5H	2.56	Theory (this work)
C_6H	3.809	Experiment (T98)
C_7H	2.97	Theory (this work)
C_8H	3.966	Experiment (T98)

NOTE.—(T98): From Taylor et al. (1998).

TABLE 2
CALCULATED VIBRATIONAL FREQUENCIES AND INTENSITIES FOR GROUND STATE ANIONS

Mode		Frequency (cm^{-1})	Intensity (cm $molec^{-1}$)
C_2H^- ($\tilde{X}\,^1\Sigma^+$); $G = 1/4$			
ν_1	σ	3376	5.68 (−20)
ν_2	σ	1888	1.37 (−17)
ν_3	π	548	3.47 (−17)
C_3H^- ($\tilde{X}\,^3A''$); $G = 3/8$			
ν_1	a'	3271	1.99 (−18)
ν_2	a'	1663	5.49 (−19)
ν_3	a'	1190	1.50 (−18)
ν_4	a'	613	1.65 (−17)
ν_5	a'	396	1.49 (−18)
ν_6	a''	427	1.72 (−19)
C_4H^- ($\tilde{X}\,^1\Sigma^+$); $G = 1/4$			
ν_1	σ	3480	1.58 (−17)
ν_2	σ	2165	1.23 (−16)
ν_3	σ	1979	7.11 (−20)
ν_4	σ	908	1.86 (−18)
ν_5	π	537	2.73 (−19)
ν_6	π	440	2.42 (−17)
ν_7	π	231	5.86 (−19)
C_5H^- ($\tilde{X}\,^3A''$); $G = 3/8$			
ν_1	a'	3441	7.39 (−18)
ν_2	a'	1896	4.80 (−17)
ν_3	a'	1793	9.36 (−19)
ν_4	a'	1477	1.38 (−18)
ν_5	a'	763	2.21 (−19)
ν_6	a'	459	2.64 (−19)
ν_7	a'	395	1.08 (−18)
ν_8	a'	195	2.52 (−17)
ν_9	a'	140	9.93 (−19)
ν_{10}	a''	457	3.09 (−19)
ν_{11}	a''	395	1.00 (−18)
ν_{12}	a''	137	4.44 (−19)
C_6H^- ($\tilde{X}\,^1\Sigma^+$); $G = 1/8$			
ν_1	σ	3480	2.58 (−17)
ν_2	σ	2222	3.02 (−16)
ν_3	σ	2142	3.72 (−20)
ν_4	σ	1979	5.53 (−17)
ν_5	σ	1207	4.67 (−18)
ν_6	σ	641	2.94 (−18)
ν_7	π	550	9.55 (−20)
ν_8	π	494	6.27 (−18)
ν_9	π	483	1.63 (−17)
ν_{10}	π	264	2.29 (−18)
ν_{11}	π	111	1.17 (−18)
C_7H^- ($\tilde{X}\,^3\Sigma^-$); $G = 3/8$			
ν_1	σ	3474	2.57 (−17)
ν_2	σ	2023	1.24 (−16)
ν_3	σ	1949	2.28 (−17)
ν_4	σ	1770	1.24 (−19)
ν_5	σ	1611	5.27 (−18)
ν_6	σ	1071	4.06 (−18)
ν_7	σ	564	8.90 (−19)
ν_8	π	487	5.35 (−20)
ν_9	π	468	1.07 (−18)
ν_{10}	π	386	2.52 (−20)
ν_{11}	π	334	2.16 (−17)
ν_{12}	π	197	2.65 (−18)
ν_{13}	π	81	1.18 (−18)
C_8H^- ($\tilde{X}\,^1\Sigma^+$); $G = 1/8$			
ν_1	σ	3480	3.53 (−17)
ν_2	σ	2231	2.71 (−18)
ν_3	σ	2200	4.44 (−16)
ν_4	σ	2096	2.70 (−16)
ν_5	σ	1982	3.48 (−17)
ν_6	σ	1354	1.58 (−19)
ν_7	σ	945	7.30 (−18)
ν_8	σ	493	3.17 (−18)
ν_9	π	550	2.25 (−19)
ν_{10}	π	529	8.24 (−18)
ν_{11}	π	513	1.27 (−17)
ν_{12}	π	460	2.06 (−19)
ν_{13}	π	275	3.08 (−19)
ν_{14}	π	165	2.68 (−18)
ν_{15}	π	64	1.07 (−18)

NOTES.—$a(-b)$ stands for $a \times 10^{-b}$. The G values refer to the ratio of the electronic degeneracy of the ground state of the anion to the overall degeneracy of the reactants.

where c is the speed of light (cm s^{-1}) and ρ is the density of vibrational states of the complex ($[cm^{-1}]^{-1}$) at an energy roughly equal to the electron affinity. In our calculations, the analytical Whitten-Rabinowitch expression is used for ρ (Holbrook et al. 1996). Here, we use degeneracy factors for k_1 but not for k_{-1}. A more complex phase-space treatment (Terzieva & Herbst 2000) would have the anion first formed in a state that correlates directly with reactants, following which rapid equilibrium would ensue between the initial state and the ground state via vibronic coupling. The anion could then only be destroyed by detachment while in the initial state, since it correlates directly with the reactants. Mathematically, the two treatments are virtually identical in the strong-coupling limit, although the more complex treatment is preferable if we must worry about specific "doorway" states (Güthe et al. 2001).

Finally, for the radiative stabilization rate k_r, we assume that the emission of one vibrational photon can stabilize the complex. The average emission rate of an individual photon in an assembly of harmonic oscillators is given approximately by the expression (Herbst 1982)

$$k_r = \frac{E_{\rm vib}}{s} \sum_{i=1}^{s} A_{1-0}^{(i)} / h\nu_i, \tag{15}$$

where $E_{\rm vib}$ is the vibrational energy with respect to the potential minimum (the electron affinity), s is the number of oscillators, $A_{1-0}^{(i)}$ is the Einstein spontaneous emission rate for the fundamental transition of the individual mode i, and the sum is over the modes i with frequencies ν_i. For vibrational energies in the range 3–4 eV, typical values of k_r are 10^2–10^3 s^{-1}. The Einstein A coefficients for the fundamental transitions of each mode can be related to the so-called radiative intensity I (cm $molecule^{-1}$) for the transition by the expression (Herbst 1982)

$$A_{1-0}^{(i)} = (8\pi/c)\nu_i^2 I. \tag{16}$$

TABLE 3

Calculated Vibrational Frequencies and Intensities for Anions in Lowest Excited States

Mode		Frequency (cm^{-1})	Intensity (cm $molec^{-1}$)
C_3H^- ($\tilde{a}\ ^1A'$) (0.13 eV; G = 1/8)			
ν_1	a'	2863	3.22 (−17)
ν_2	a'	1854	6.57 (−18)
ν_3	a'	1140	3.88 (−19)
ν_4	a'	1030	6.40 (−18)
ν_5	a'	427	2.17 (−18)
ν_6	a''	299	4.11 (−18)
C_4H^- ($\tilde{a}\ ^3A''$) (2.77 eV; G = 3/4)			
ν_1	a'	2922	5.51 (−17)
ν_2	a'	1914	2.66 (−18)
ν_3	a'	1586	6.22 (−18)
ν_4	a'	961	3.12 (−19)
ν_5	a'	954	1.57 (−18)
ν_6	a'	449	3.60 (−18)
ν_7	a'	186	8.59 (−19)
ν_8	a''	473	9.58 (−18)
ν_9	a''	302	5.22 (−18)
C_5H^- ($\tilde{a}\ ^1A'$) (0.31 eV; G = 1/8)			
ν_1	a'	2995	2.28 (−17)
ν_2	a'	1992	5.54 (−17)
ν_3	a'	1914	5.31 (−18)
ν_4	a'	1407	2.49 (−18)
ν_5	a'	884	2.51 (−17)
ν_6	a'	762	8.18 (−19)
ν_7	a'	427	2.18 (−19)
ν_8	a'	402	2.94 (−18)
ν_9	a''	610	8.65 (−19)
ν_{10}	a''	310	2.97 (−19)
ν_{11}	a''	152	3.84 (−18)
ν_{12}	a''	131	1.57 (−18)
C_6H^- ($\tilde{a}\ ^3A''$) (2.29 eV; G = 3/8)			
ν_1	a'	3001	3.57 (−17)
ν_2	a'	1978	1.33 (−18)
ν_3	a'	1861	1.81 (−17)
ν_4	a'	1653	1.04 (−17)
ν_5	a'	1197	2.16 (−18)
ν_6	a'	808	5.59 (−17)
ν_7	a'	649	6.61 (−19)
ν_8	a'	389	2.63 (−19)
ν_9	a'	347	1.13 (−18)
ν_{10}	a'	228	5.86 (−19)
ν_{11}	a'	94	1.43 (−18)
ν_{12}	a''	579	3.57 (−19)
ν_{13}	a''	449	3.99 (−22)
ν_{14}	a''	260	1.90 (−18)
ν_{15}	a''	114	1.85 (−18)
C_7H^- ($\tilde{a}\ ^1A'$) (0.43 eV; G = 1/8)			
ν_1	a'	3118	1.05 (−17)
ν_2	a'	2077	1.59 (−16)
ν_3	a'	1996	4.57 (−19)
ν_4	a'	1834	2.33 (−17)
ν_5	a'	1569	6.10 (−18)
ν_6	a'	1078	8.76 (−18)
ν_7	a'	698	6.79 (−17)
ν_8	a'	567	2.74 (−18)
ν_9	a'	441	7.76 (−19)
ν_{10}	a'	416	8.35 (−18)
ν_{11}	a'	394	9.22 (−20)
ν_{12}	a'	175	9.35 (−19)
ν_{13}	a'	70	1.01 (−18)
ν_{14}	a''	613	2.74 (−18)
ν_{15}	a''	555	8.95 (−20)
ν_{16}	a''	321	2.07 (−19)
ν_{17}	a''	205	5.58 (−19)
ν_{18}	a''	81	3.67 (−18)
C_8H^- ($\tilde{a}\ ^3A''$) (1.97 eV; G = 3/8)			
ν_1	a'	3133	1.60 (−17)
ν_2	a'	1986	3.63 (−17)
ν_3	a'	1943	7.29 (−20)
ν_4	a'	1906	5.49 (−17)
ν_5	a'	1717	2.74 (−18)
ν_6	a'	1386	6.30 (−18)
ν_7	a'	954	7.29 (−18)
ν_8	a'	669	1.03 (−16)
ν_9	a'	500	2.13 (−18)
ν_{10}	a'	403	1.95 (−19)
ν_{11}	a'	397	3.68 (−18)
ν_{12}	a'	363	1.18 (−19)
ν_{13}	a'	271	2.70 (−19)
ν_{14}	a'	151	7.60 (−19)
ν_{15}	a'	64	1.05 (−18)
ν_{16}	a''	587	9.67 (−20)
ν_{17}	a''	546	2.28 (−19)
ν_{18}	a''	429	4.61 (−19)
ν_{19}	a''	284	4.24 (−19)
ν_{20}	a''	168	1.27 (−18)
ν_{21}	a''	67	1.52 (−18)

Notes.—$a(-b)$ stands for $a \times 10^{-b}$. The energies of the excited electronic states are given next to the state description and include zero-point energies. The G values refer to the ratio of the electronic degeneracy of the excited state of the anion to the overall degeneracy of the reactants.

Tables 1, 2, and 3 contain the information needed for our calculations of radiative attachment rates. In Table 1, we list the electron affinities used. For the C_nH anions with n even, the experimental values of Taylor et al. (1998) are chosen. Our newly calculated values lie below the experimental ones by 0.2–0.4 eV. For n odd, our calculated values of 1.93 eV ($n = 3$), 2.56 eV ($n = 5$), and 2.95 eV ($n = 7$) are in excellent agreement with the prior values of Blanksby et al. (2001). Other experimental and theoretical studies involving the C_nH species and their anions have been conducted by Feher & Maier (1994), Mölder et al. (2001), and Pan et al. (2003). Table 2 contains the calculated vibrational frequencies and radiative intensities I for the anions in their ground electronic states, while Table 3 contains the same information for the first excited electronic states, the calculated energy of which contains zero-point energy corrections. G-values are listed for each anion state. Note that the excited state of C_2H^- is too high in energy to be included, since it lies above C_2H. In the current radiative attachment calculations, the excited states were excluded for a variety of reasons for all species except C_3H, where the first excited anion state is nearly degenerate with the ground state. For the case of C_4H^- formation, the first excited state, a triplet, has its minimum potential at a bent configuration. If we assume that the initial attachment must occur in the linear configuration, the

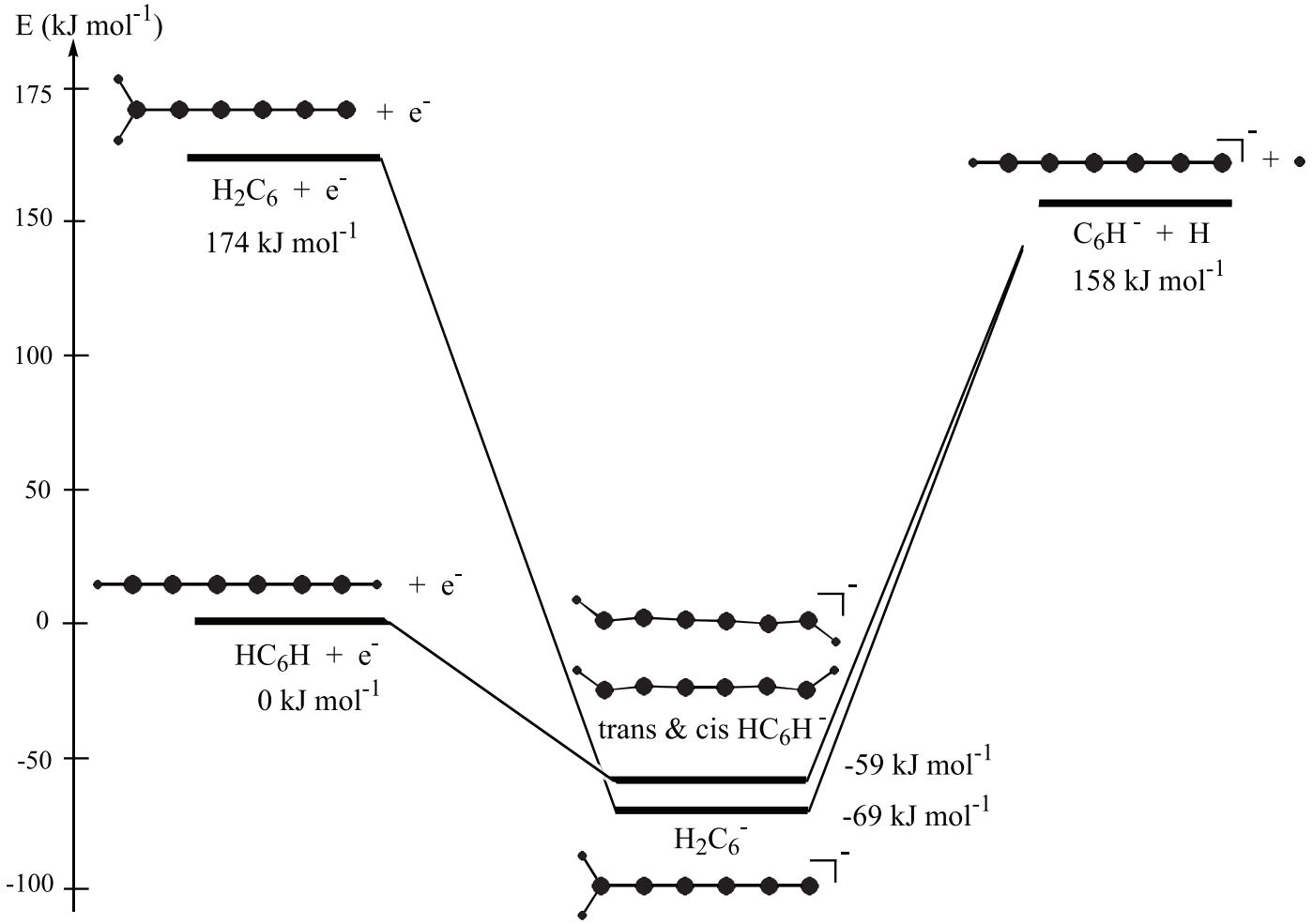

FIG. 1.—Potential energy surface for dissociative attachment of H_2C_6 and HC_6H. Energies are in kJ mol^{-1}; 1 kJ $mol^{-1} = 1.036 \times 10^{-2}$ eV = 120.3 K.

triplet state of the anion is sufficiently high in energy that it cannot be reached by low-energy electrons. The situation is not the same for C_6H^- and C_8H^- formation, but since the attachment of these ions occurs at the collisional rate anyway, additional states will not affect the result significantly. For the case of C_5H^-, the ground electronic state, of symmetry $^3A''$, and the first excited state, of symmetry $^1A'$, also show potential minima at bent configurations, although their energies at the linear configuration are still low enough that the states can be accessed. Although the $^1A'$ state lies only 0.31 eV above the ground state, it was not included in the calculation because its degeneracy is only 1/3 that of the ground state and its density of vibrational states is comparable. A similar story holds for the case of C_7H^-. Nevertheless, all excited state results except for C_2H^- are reported in case they are needed in future, more detailed calculations.

3.1. *Dissociative Attachment: A More Detailed Look*

How rapid are exothermic dissociative attachment processes? If the dissociative attachment of the anionic complex into products is much more rapid than auto-detachment or radiative attachment, then the rate coefficient for dissociative attachment is simply given by k_1. Indeed, studies of exothermic dissociative attachment at 300 K show that rate coefficients in the range 5×10^{-8}–3.5×10^{-7} cm^3 s^{-1} are possible (Adams et al. 1986). These large values do not always occur, as can be seen by a number of such reactions, such as

$$e^- + Cl_2 \longrightarrow Cl^- + Cl, \qquad (17)$$

that appear to have activation energy barriers (Petrie 1996). These activation energy barriers need not arise from repulsive potentials as in normal chemical reactions between heavy species, since the electron affinity of the neutral species leading to the intermediate complex in reaction (17) is large. To start to elucidate the problem, we have looked a little more carefully at reaction (5) and show the relevant ground-state potential surfaces for dissociative attachment of H_2C_6 and HC_6H in Figure 1. The former is calculated to be exothermic by 16 kJ mol^{-1}, while the latter is quite endothermic (158 kJ mol^{-1}). The ground electronic state of $H_2C_6^-$ lies 243 kJ mol^{-1} (2.52 eV) below the neutral carbene and 227 kJ mol^{-1} (2.35 eV) below the ground-state products $C_6H^- + H$.

Although it would appear that there is no barrier to the exothermic process of dissociative attachment of H_2C_6, the figure does not really indicate the detailed mechanism of reaction. If dissociative attachment is analogous to the "direct" mechanism for dissociative recombination of positive molecular ions, then the reaction proceeds not through the strongly bound ground electronic state of the intermediate anion but through an excited electronic state that is sufficiently repulsive to interact with the potential of the neutral H_2C_6 near its equilibrium geometry (Florescu-Mitchell & Mitchell 2006). Without a calculation of possible excited anionic states, we cannot determine the mechanism of exothermic dissociative attachment reactions and whether or not they occur rapidly. Note that although the radiative attachment of electrons to H_2C_6 is exothermic by 2.52 eV (the electron affinity), radiative stabilization of the complex is not likely to be competitive with detachment, because radiative stabilization rates are normally rather

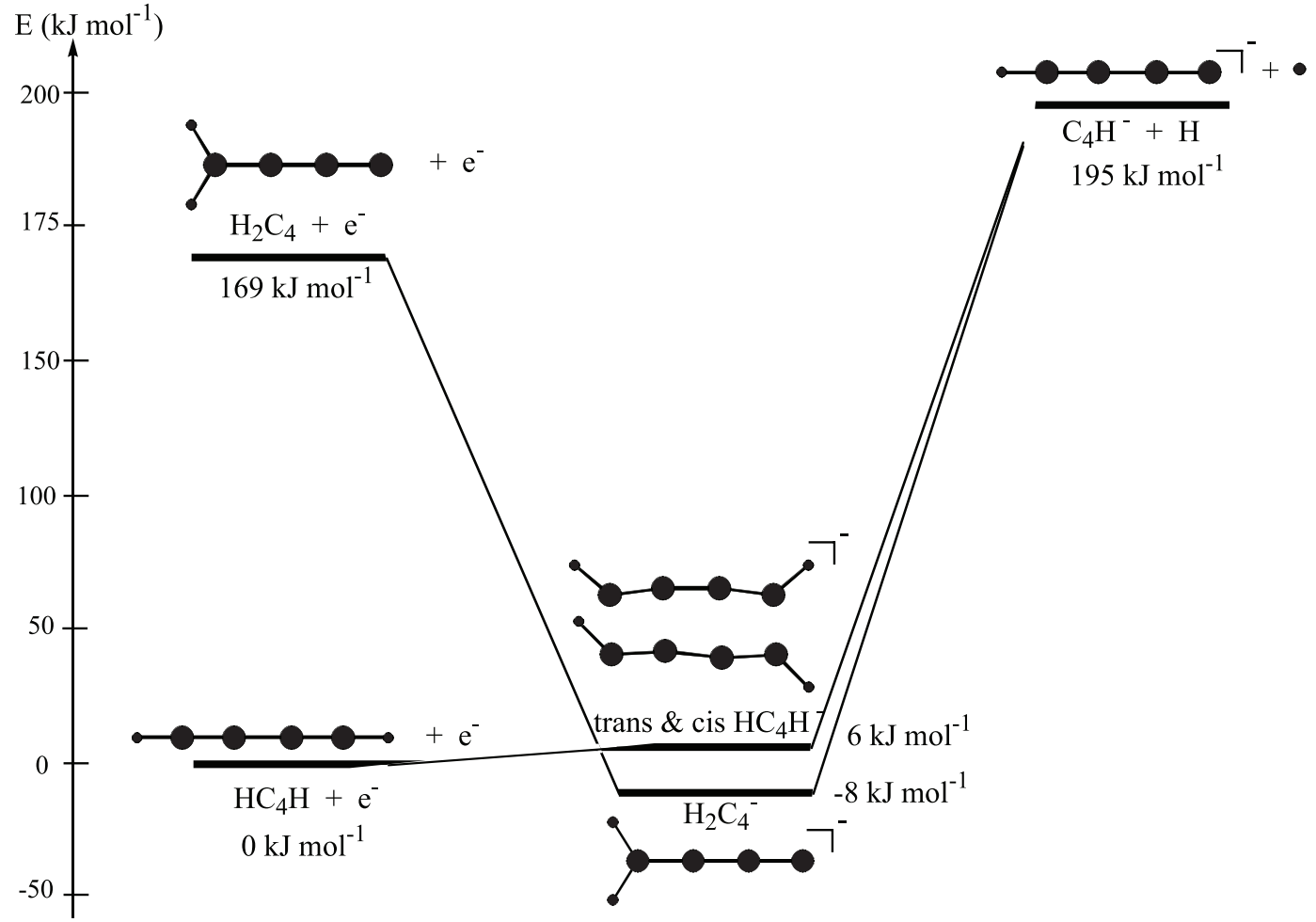

FIG. 2.—Potential energy surface for dissociative attachment of H_2C_4 and HC_4H. Energies are in kJ mol^{-1}; 1 kJ mol^{-1} = 1.036 × 10^{-2} eV = 120.3 K.

slow ($\approx 10^2$–10^3 s^{-1}) compared with complex detachment involving superthermal energies. Analogous figures for the dissociative attachment reactions of H_2C_4 and H_2C_8 are shown in Figures 2 and 3, respectively. The dissociative attachment of H_2C_4 is endothermic and does not occur under cold interstellar and circumstellar conditions. In all three figures, one can see that the associative detachment reactions of the C_nH^- anions ($n = 4$,6, 8) with atomic hydrogen proceed quite exothermically to the normal polyacetylene structure HC_nH and electrons. The $n = 4$ and $n = 6$ reactions have been studied in the laboratory by Eichelberger et al. (2007) and occur rapidly, a fact that offers indirect evidence that the dissociative attachments are also rapid. Although Eichelberger et al. (2007) also report associative pathways to form stabilized complexes, the mechanism is not radiative at the densities of their experiment.

4. RESULTS AND DISCUSSION

Our calculated new results for k_r, k_{-1}, and the overall radiative attachment rate coefficients are shown in Table 4, along with the estimated results for $k_{\rm ratt}$ used by Millar et al. (2007) and some new results of Agúndez et al. (2008) from simple models fit to observational results. It can be seen that our new rate coefficients are larger than the previous estimates for C_4H^- and C_5H^- formation. The differences arise mainly from significantly larger values of the radiative emission rate coefficient k_r compared with our previous estimate of $k_r \approx 10^2$ s^{-1} and from an error in the previous calculation of the density of states for C_5H^-. The result for the formation of C_6H^- is unchanged, because the density of states is so large that the rate coefficient for radiative attachment is just the collisional rate coefficient k_1 with the appropriate G factor. The rate coefficients for radiative attachment of all larger anions of the form C_nH^- also occur at the collisional rate, but differ according to whether n is even or odd because of different values of G (Millar et al. 2007). The results of Agúndez et al. (2008) show that observations are fit best by a significantly lower value of $k_{\rm ratt}$ for the attachment of electrons to C_4H, while our values for C_6H and C_8H are more acceptable (see below). As regards the very small anions in this family, the calculated attachment rate coefficients are indeed tiny; that for C_2H^- is considerably below the upper limit of Agúndez et al. (2008).

With the increase in the calculated attachment rate coefficients for C_4H^- and C_5H^-, predicted anion-to-neutral abundances ratios for these radicals are likely to go up linearly. This assumption stems from the simple steady-state relation

$$[C_nH^-]/[C_nH] = k_{\rm ratt}[e^-]/D, \qquad (18)$$

where D is the anion destruction rate, and the argument that D and the electron abundance are not affected by the increase in $k_{\rm ratt}$. Table 5 shows the old (model) and new calculated C_4H^-/C_4H abundance ratios for TMC-1, IRC +10216, and L1527 using this assumption and compares these values with observations. For TMC-1, the older value for the attachment rate coefficient leads to an abundance ratio of 0.0013 at early time (and one at 0.0019

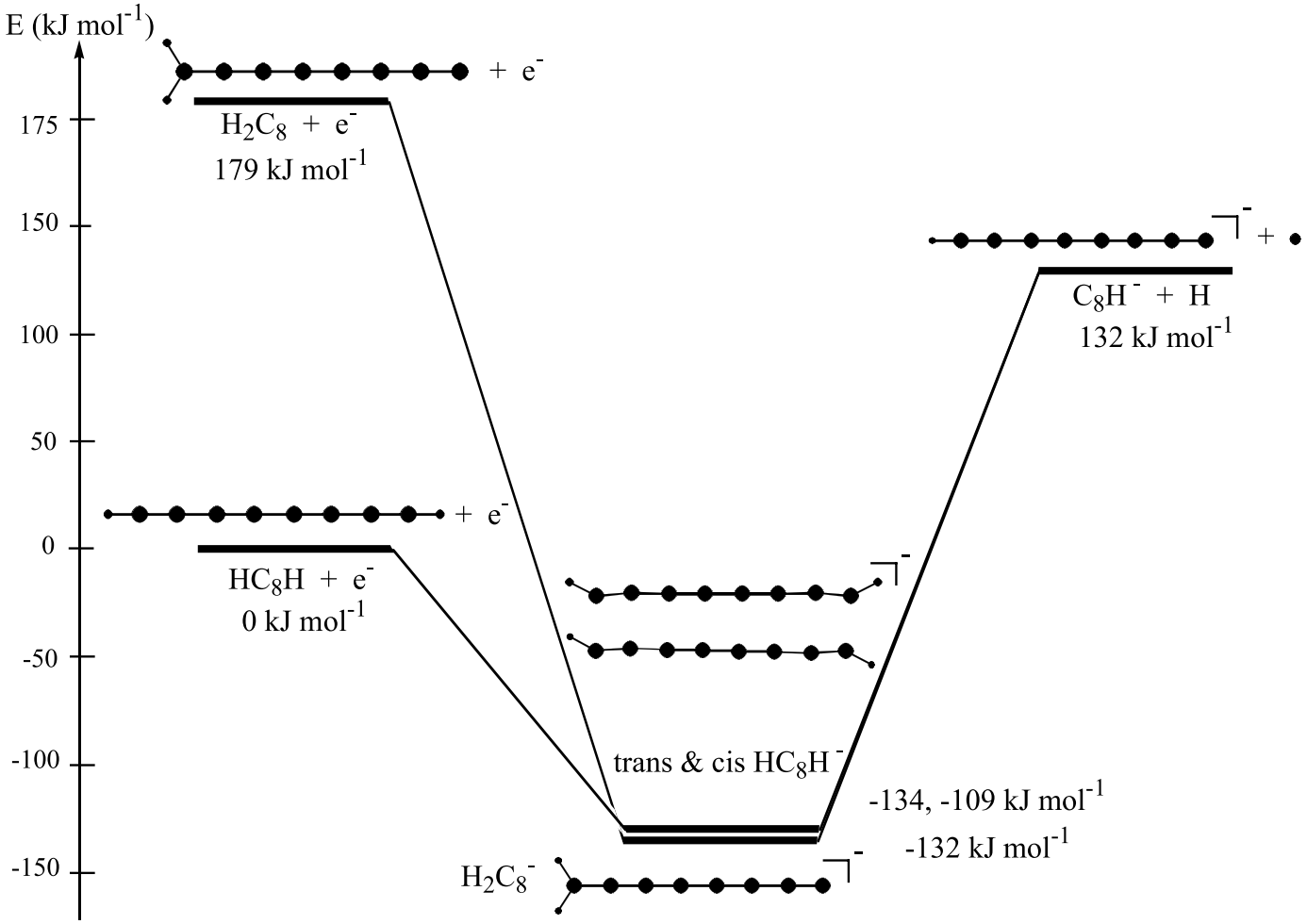

FIG. 3.—Potential energy surface for dissociative attachment of H_2C_8 and HC_8H. Energies are in kJ mol^{-1}; 1 kJ mol^{-1} = 1.036×10^{-2} eV = 120.3 K.

at steady state; Millar et al. 2007) in comparison with an observed upper limit of 5.2×10^{-5} (Brünken et al. 2007; Agúndez et al. 2008). The new result makes the disagreement worse by a factor of 5.5, leading to a prediction for the anion-to-neutral abundance ratio too large by at least a factor of ≈100. For IRC +10216, the ratio of anion to neutral column densities was calculated to be 0.0077 by Millar et al. (2007), but this value rose to 0.038 in a refined calculation designed to improve agreement with overall column densities of C_6H, C_8H, and their anions rather than the anion-to-neutral abundance ratio (Remijan et al. 2007). This new result is ≈150 times greater than the observed ratio of 2.4×10^{-4}. Here, too, an increase of the attachment rate coefficient for C_4H further worsens the already poor agreement for the anion-to-neutral column-density ratio by a factor of 5.5. The earlier conclusion by Cernicharo et al. (2007) that the rate of radiative attachment to C_4H is much smaller than that calculated by phase-space theory seems inescapable. But since the C_4H^- anion is present in IRC +10216 despite the fact that it cannot be formed exothermically

TABLE 4
CALCULATED RADIATIVE ATTACHMENT RESULTS

Radical	k_r (s^{-1})	k_{-1} (s^{-1})	k_{ratt} (300 K)	k_{ratt} (300 K, est)	k_{ratt} (300 K, A08)
C_2H	288	1.76 (10)	2.0 (−15)	...	<1.5 (−11)
C_3H	39	9.25 (08)	1.7 (−14)	...	...
C_4H	746	7.36 (03)	1.1 (−08)	2.0 (−09)	9 (−11)
C_5H	164	5.83 (02)	4.1 (−08)	9.0 (−10)	...
C_6H	1304	2.97 (−02)	6.2 (−08)	6.0 (−08)	1.4 (−08)
C_7H	...	...	1.9 (−07)	2.0 (−07)	...
C_8H	...	...	6.2 (−08)	6.0 (−08)	2.5 (−08)

NOTES.—The radiative attachment rate coefficients have units cm^3 s^{-1}. Our result for C_3H includes the two lowest states of C_3H^-, although k_r and k_{-1} for only the ground state of the anion are shown. The estimated results are from Millar et al. (2007), while the results labeled A08 are from Agúndez et al. (2008). The temperature dependence is $(T/300)^{-1/2}$.

TABLE 5
Comparison of Theory and Observation for C_4H^-/C_4H

Source	Observation	Model Results	Adjusted Value	Model Reference
TMC−1	<5.2(−5)	0.0013	0.007	Mi07
IRC +10216	2.4(−4)	0.0077	0.04	Mi07
IRC +10216	2.4(−4)	0.038	0.21	Re07
L1527	1.1(−4)	0.1	0.1	HH

Notes.—The model results are from Millar et al. (2007; Mi07), Remijan et al. (2007; Re07), and Harada & Herbst (2008; HH). The TMC-1 results are at early-time, while the IRC +10216 results are for a fractional abundance of acetylene of 1×10^{-5}. The new L1527 results of HH use the newly calculated value for the radiative recombination rate coefficient, and so need not be adjusted. For a compilation of observational references, see Agúndez et al. (2008).

TABLE 6
Calculated Vibrational Frequencies and Intensities for Ground-State C_3N Anion

Mode		Frequency (cm^{-1})	Intensity (cm $molec^{-1}$)
C_3N^- ($\tilde{X}\ ^1\Sigma^+$); $G = 1/4$			
ν_1	σ	2261	1.00 (−16)
ν_2	σ	2025	5.24 (−18)
ν_3	σ	903	1.10 (−18)
ν_4	π	568	3.80 (−18)
ν_5	π	224	4.78 (−18)

Notes.—a ($-b$) stands for $a \times 10^{-b}$; the G value refers to the ratio of the electronic degeneracy of the ground state of the anion to the overall degeneracy of the reactants.

by dissociative attachment, there seems no alternative to radiative attachment, albeit at a much lower rate than predicted here. A more detailed theoretical treatment is clearly needed, possibly involving dipole-bound states (see below). The failure of the phase-space approach is confirmed by comparison of the newly observed C_4H^-/C_4H abundance ratio in L1527 (Sakai et al. 2008; Agúndez et al. 2008) with gas-phase model results for this source that utilize the new value for $k_{\rm ratt}$ (Harada & Herbst 2008). At the time of best agreement with the 20+ species seen in this source, the model obtains a ratio of ≈0.1, which is nearly 1000 times too large compared with observation.

The very poor agreement between observational and theoretical results for the C_4H^-/C_4H abundance ratio can be improved some by a change in the observational analysis of the neutral C_4H. As noted by the referee, all observed column densities of C_4H are based on a theoretically determined dipole moment of 0.9 Debye, which is the proper value for an isolated $^2\Sigma$ ground state. However, the *isolated* low-lying $^2\Pi$ excited state possesses a much larger theoretical dipole moment of 4.4 Debye (Woon 1995), and assorted experiments, such as laser-induced fluorescence spectroscopy (Hoshina et al. 1998), show a mixing between the two states such that the $^2\Pi$ character of the ground state is about 40%. This mixing will lead to a mixed ground state with a dipole significantly higher than 0.9 Debye, and a higher effective moment will lead to a lower column density for C_4H. Nevertheless, the discrepancy between observation and theory will be lessened, not removed. The existence of a larger dipole than 0.9 Debye in the mixed ground state of C_4H also complicates the situation for the radiative attachment of C_4H^-, since a dipole-bound state and associated resonances may exist and be accessible to thermal electrons.

For the cases of C_6H^- and C_8H^-, the ions can be produced via electron attachment or dissociative attachment from the precursor carbenes. Model results for TMC-1 (Millar et al. 2007) and IRC +10216 (Millar et al. 2007; Remijan et al. 2007) have been undertaken without the latter possibility. Neither set of results is changed by the calculations reported here. The TMC-1 results are in good agreement with observation both for column density and anion-to-neutral ratio at early times (Millar et al. 2007; Brünken et al. 2007), but the situation for IRC +10216 is more complex. Better agreement with overall column densities of anion and neutral was obtained by Remijan et al. (2007) compared with Millar et al. (2007), at the expense of an overestimation of the anion-to-neutral abundance ratio.

The inclusion of dissociative attachment reactions further complicates the situation. Although these latter reactions are exothermic, it is unclear whether they occur with the collisional rate coefficient or a smaller one. Experimental and/or theoretical studies are clearly needed, although they will not be facile. The competition between radiative electron attachment and dissociative attachment in the formation of C_6H^- has been investigated for the case of L1527 by Sakai et al. (2007), who defined an effective rate coefficient $k_{\rm eff}$ by the equation

$$k_{\rm eff} = k_c(f + [H_2C_6]/[C_6H]) \quad (19)$$

where f is the fraction of the collisional rate coefficient at which the attachment reaction proceeds, and it is assumed that dissociative attachment occurs at the collisional rate coefficient (labeled k_c by Sakai et al. 2007). Based on observed abundances of the anion and its two precursor neutrals, Sakai et al. (2007) concluded that a value of $f \sim 1$, which is obtained by phase-space theory, would produce too much C_6H^- by perhaps an order of magnitude. Using a similar type of analysis for TMC-1, where the abundance ratio of H_2C_6 to C_6H is smaller (0.06) than in L1527 (0.24), we estimate that the total neglect of radiative attachment ($f = 0$) would lead to a calculated abundance ratio between anion and neutral a factor of ≈5 below the observed value, while the use of $f = 1$ leads to a calculated abundance ratio too large by a factor of 2–3 (Millar et al. 2007). It is likely that both radiative and dissociative attachment contribute. A similar analysis cannot be done for the case of C_8H^-, since the precursor carbene has not been detected. It will be interesting to include the carbenes in detailed chemical models of assorted sources, so that the role of dissociative attachment can be better quantified.

The most recent detection of C_3N^- in IRC +10216 has prompted us to recalculate the value of the radiative attachment rate coefficient of C_3N. Using the methods discussed here and the data listed in Table 6, along with a theoretical electron affinity of 4.37 eV, we obtain a 300 K value for the rate coefficient of 2.63×10^{-10} cm^3 s^{-1}, which is in excellent agreement with the earlier value of Petrie & Herbst (1997). With this rate coefficient and with the assumption that reaction (4) occurs rapidly, a simple model does not predict a sufficient amount of C_3N^- to explain the observation (M. Guélin 2007, private communication). Given the low observed abundance of HNCCC in IRC +10216 (Thaddeus et al. 2008), it would seem that the radiative attachment rate coefficient calculated here is too low, perhaps by an order of magnitude.

We thank the referee for a detailed reading of our paper. E. H. acknowledges the support of the NSF for his research program in astrochemistry.

REFERENCES

Adams, N. G., Smith, D., Viggiano, A. A., Paulson, J. F., & Henchman, M. J. 1986, J. Chem. Phys., 84, 6728
Agúndez, M., Cernicharo, J., Guélin, M., Gerin, M., McCarthy, M. C., & Thaddeus, P. 2008, A&A, 478, L19
Becke, A. D. 1993, J. Chem. Phys., 98, 5648
Blanksby, S. J., McAnoy, A. M., Dua, S., & Bowie, J. H. 2001, MNRAS, 328, 89
Brünken, S. Gupta, H., Gottlieb, C. A., McCarthy, M. C., & Thaddeus, P. 2007, ApJ, 664, L43
Cernicharo, J., Guélin, M., Agúndez, M., Kawaguchi, K., McCarthy, M., & Thaddeus, P. 2007, A&A, 467, L37
Christophorou, L G. 1983, Electron-Molecule Interactions and Their Applications, ed. L. G. Christophorou (Singapore: Academic Press)
Dunning, T. H. 1989, J. Chem. Phys., 90, 1007
Eichelberger, B., Snow, T. P., Barckholtz, C., & Bierbaum, V. M. 2007, ApJ, 667, 1283
Feher, M., & Maier, J. P. 1994, Chem. Phys. Lett., 227, 371
Florescu-Mitchell, A. I., & Mitchell, J. B. A. 2006, Phys. Rep., 430, 277
Frisch, M. J., et al. 2001, GUASSIAN 98 Revision, A.11 (Pittsburgh: Gaussian Inc.)
Graupner, K., Merrigan, T. L., Field, T. A., Youngs, T. G. A., & Marr, P. C. 2006, New J. Phys., 8, 117
Gupta, H. C., Brünken, S., Tamassia, F., Gottlieb, C. A., McCarthy, M. C., & Thaddeus, P. 2007, ApJ, 655, L57
Güthe, F., Tulej, M., Pachkov, M. V., & Maier, J. P. 2001, ApJ, 555, 466
Harada, N., & Herbst, E. 2008, ApJ, submitted
Herbst, E. 1981, Nature, 289, 656
———. 1982, Chem. Phys., 65, 185
———. 1985, A&A, 153, 151
Herzberg, G. 1966, Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules (New York: D. van Nostrand)
Holbrook, K. A., Pilling, M. J., & Robertson, S. H. 1996, Unimolecular Reactions (New York: John Wiley & Sons)
Hoshina, K., Kohguchi, H., Ohshima, Y., & Endo, Y. 1998, J. Chem. Phys., 108, 3465
Kasai, Y., Kagi, E., & Kawaguchi, K. 2007, ApJ, 661, L61
Kawaguchi, K., et al. 2007, PASJ, 59, L47
Lee, C., Yang, W., & Parr, R. G. 1988, Phys. Rev. B., 37, 785
McCarthy, M. C., Gottlieb, C. A., Gupta, H. C., & Thaddeus, P. 2006, ApJ, 652, L141
Millar, T. J., Herbst, E., & Bettens, R. P. A. 2000, MNRAS, 316, 195
Millar, T. J., Walsh, C., Cordiner, M. A., Ní Chuimí, R., & Herbst, E. 2007, ApJ, 662, L87
Mölder, U., Bruk, P., & Koppel, I. A. 2001, Int. J. Quant. Chem., 82, 73
Pan, L., Rao, B. K., Gupta, A. K., Das, G. P., & Ayyub, P. 2003, J. Chem. Phys., 119, 7705
Petrie, S. 1996, MNRAS, 281, 137
Petrie, S., & Herbst, E. 1997, ApJ, 491, 210
Remijan, A. J., Hollis, J. M., Lovas, F. J., Cordiner, M. A., Millar, T. J., Markwick-Kemper, A. J., & Jewell, P. R. 2007, ApJ, 664, L47
Sakai, N., Sakai, T., Osamura, Y., & Yamamoto, S. 2007, ApJ, 667, L65
Sakai, N., Sakai, T., & Yamamoto, S. 2008, ApJ, 673, L71
Taylor, T. R., Cangshan, X., & Neumark, D. M. 1998, J. Chem. Phys., 108, 10018
Terzieva, R., & Herbst, E. 2000, Int. J. Mass Spectrom., 201, 135
Thaddeus, P., Gottlieb, C. A., Gupta, H., Brünken, S., McCarthy, M. C., Agúndez, M., Guélin, M., & Cernicharo, J. 2008, ApJ, 677, 1132
Woodin, R. L., Foster, M. S., & Beauchamp, J. L. 1980, J. Chem. Phys., 72, 4223
Woon, D. E. 1995, Chem. Phys. Lett., 244, 45